The Relevance of Printing Processes in Proton Exchange Membrane Fuel Cell Manufacturing

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The present study compares these processes on three main fields, (i) catalyst layers manufacturability, detailing the specific protocols that are required to produce catalyst layers, (ii) catalyst layers quality, analyzing the typical deposition defects of the catalyst layers induce by the process, (iii) catalyst layers economic issue, where manufacturing processes are compared as a function of the production costs.

Conventional printing defects appear on the catalyst layers made by printing processes. However, the tested catalyst layers show no significant electrochemical difference. In a context of an increasing market estimated to reaches $1.2 billion by 2014, each process suits for a specific type of production depending technical and economical requirements.

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1 INTRODUCTION

The hydrocarbon economy is based on the petroleum use as the primary power source. It emits carbon dioxide and other pollutants, fossil energies are limited and the energy demand increases. In such a context, a replacement primary energy source is required and the "Hydrogen economy" has been proposed. The paternity of this concept is attributed to John O'M. Bockris, Professor of Chemistry at Texas A&M University and to Edward Justi a Physics Professor at the University of Hannover in the 1970s. The hydrogen economy was described as an economy based on the use of hydrogen to transport energy from renewable sources (Bockris, 2002). Hydrogen would have been used in fuel cell to produce electricity and as a replacement to natural gas with no pollutant production (Veziroglu 2000) especially any carbon dioxide formation (Bockris 2008). Since, the concern into Hydrogen economy has grown up, the concept has been accepted, research is made, and development and commercialization are progressing (Lattina and Utgikar 2007). The hydrogen economy is based on the cycle presented in figure 1, where water and primary energies sources produce hydrogen.

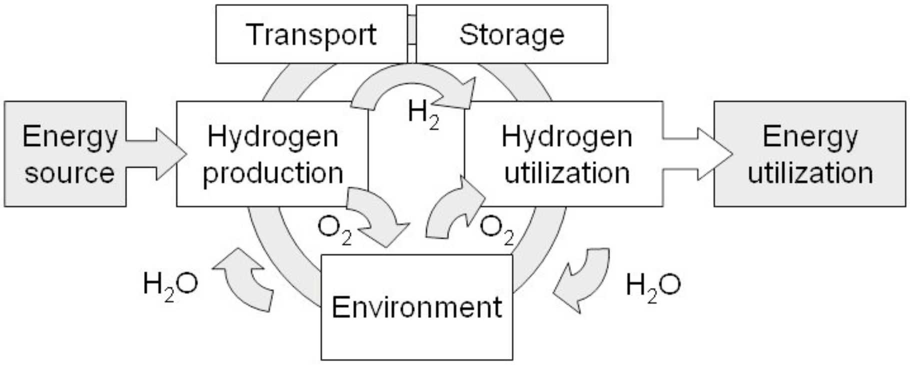


Figure 1: *Hydrogen cycle*

The hydrogen cycle describes how the water is recycled in our planet thought the equation of water production (1).

$$H_2 0 + energy \leftrightarrow \frac{1}{2} O_2 + H_2 \qquad (1)$$

The water decomposition requires energy to produces dioxygen and dihydrogen. At the opposite the formation of water from dioxygen and dihydrogen gives some energy back. Hydrogen carries energy for electricity generation, transportation and residential, commercial and industry needs. This cycle is based on three main components; two of them; water and dioxygen, are components that are widely present in the environment. Then, hydrogen allows the transportation of the energy given for the reaction takes place, in ISO 13600 standards, it is considered as an energy carrier. It is an intermediate medium for storing and delivery energy in a usable form and it has limited environmental impacts. The transition to an all-hydrogen powered economy will affect the entire humankind and consequently, the concept of hydrogen civilization has been proposed (Goltsova and Veziroglu, 2001).

The Hydrogen economy concept does not reach the total agreement of the scientific community. Some authors highlight limitations on the real potential of such an energy carrier (Bossel, 2006):

- the production, storage and transportation of hydrogen require energy that is lost when the hydrogen is converted into energy into the fuel cell
- The use of clean water as a primary source of hydrogen production will increase the water needs. Unfortunately, obtaining clean water is already a main concern for populations worldwide.
- The use of expensive and rare materials in the fuel cells limits the development of a mass-production.

The implementation of hydrogen as an energy carrier is a journey rife with difficulties (Kumar, Britter and Gupta, 2009) that began 150 years ago when Sir William Groves discovered the fuel cell principle in 1839.

Fuel cells are composed by different cells in which three main components are required:

- Two electrodes: a cathode and an anode, where the electrochemical reactions take placed. They produce negative and positive charges holders (depending on the fuel cell types)
- And an electrolyte placed in between, that allow the specific diffusion of chosen elements from one side to another of the cell.

From the original fuel cell made by Sir Groves, five types of fuel cells technologies have been developed. Their name generally described the electrolyte they incorporate:

- Solid Oxide Fuel Cell (SOFC)
- Molten Carbonate Fuel Cell (MCFC)
- Phosphoric Acid Fuel Cell (PAFC)
- Alkaline Fuel Cell (AFC)
- Proton Exchange Membrane Fuel Cell (PEMFC).

They have specific electrochemical reactions, operating conditions and especially different economical characteristics (table 1).

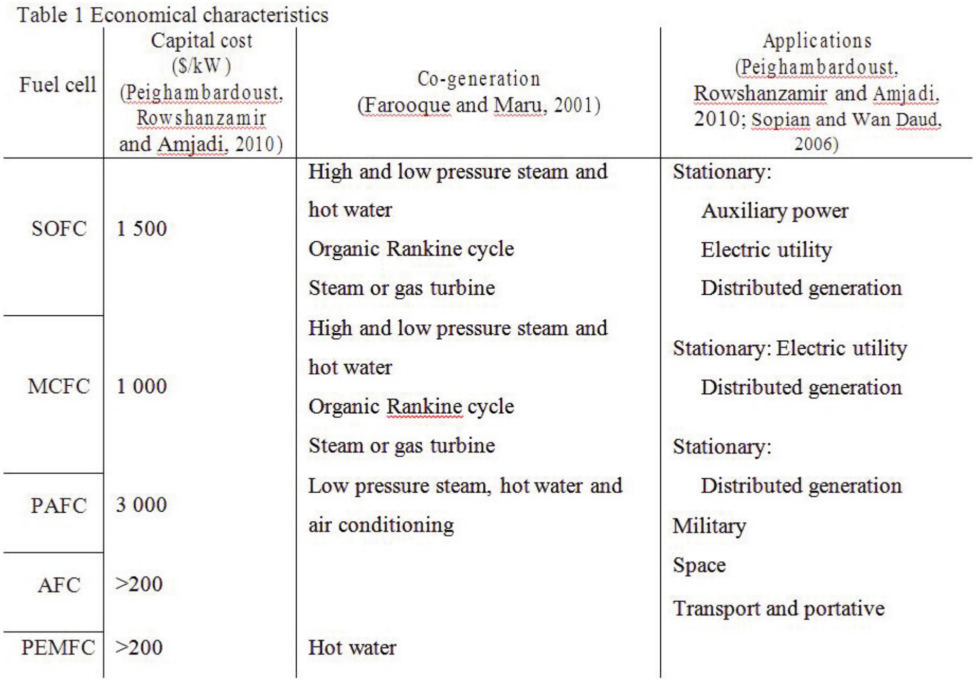


Table 1 Economical characteristics

Fuel cell	Capital cost ($/kW) (Peighambardoust, Rowshanzamir and Amjadi, 2010)	Co-generation (Farooque and Maru, 2001)	Applications (Peighambardoust, Rowshanzamir and Amjadi, 2010; Sopian and Wan Daud, 2006)
SOFC	1 500	High and low pressure steam and hot water Organic Rankine cycle Steam or gas turbine	Stationary: Auxiliary power Electric utility Distributed generation
MCFC	1 000	High and low pressure steam and hot water Organic Rankine cycle Steam or gas turbine	Stationary: Electric utility Distributed generation
PAFC	3 000	Low pressure steam, hot water and air conditioning	Stationary: Distributed generation Military
AFC	>200		Space
PEMFC	>200	Hot water	Transport and portative

Table 1: *Economical characteristics*

Objectives of the present work

Due to its lower cost of production compared to the other technologies and its huge application potential for both transport and portative, the PEMFC is the technology targeted in this article. The reduction of the cost of the power produced by the PEMFC is the points where converge the research and development efforts (Sopian and Wan Daud, 2006).

The fuel cell is composed by a stack of cells. The cells are the core of the fuel cell and convert the reactive gases (hydrogen and oxygen) into electricity in catalyst layers. The electrochemical reactions that take placed require specific, rare and expensive material. Thereby, numerous research works focus on the decreases of their manufacturing cost as a priority. These MEAs components are commonly manufactured by blade coating or spray techniques by the deposition of a dispersion of carbon supported platinum and a specific ionomer called Nafion®. The deposition of this dispersion by blade coating or spray requires similar formulation than those used by printing processes. Consequently, the authors postulate that the use of conventional printing processes for manufacturing fuel cell components will offer new opportunities.

Besides, the printing techniques use is extending for new applications: electronics components manufacturing. This new field is called the printed electronics.

In this article, three printing processes, screen printing, ink jet and flexography are likened to the spray and blade coating techniques. These five deposition processes are compared as regards to the technical and commercial requirement of the PEM fuel cell.

Hence, the impact of each process on the components surface structure is observed. The electrochemical performances of fuel cells made with the different techniques are measured. Finally, the article highlights the adequacy between the deposition technologies and the fuel cell markets and applications. It allows quantifying the relevance of the printing processes, expending fuel cell opportunities and promoting printing processes.

2 Printing electronics: a new way to manufacture Fuel cell components?

Printed electronics is a technology of surface functionalization that links microelectronics, chemistry and printing fields. It is based on the use of conventional printing processes that allows the manufacture of electronic system without requiring expensive and sensitive silicon-based material (Perelaer et al., 2010). With manufacturing by printing processes, substrates can be functionalized even they are flexible, porous, rough or fragile.

2.1 Printing processes characteristics

The printing processes differ by their resolution and run characteristics that are detailed in table 2. The resolution of the process, which refers to the precision and the accuracy of the process, is a major parameter for printed electronics manufacturing.

Processes	Flexography	Gravure	Offset	Screen printing	Ink jet
Printing form	Cliché	Engraved cylinder	Plate	Screen	No printing form
Resolution (dpi)	150	200	200 -300	120	600
(mm)	0.16	0.1	0.1	0.2	0.04
Optimal run length (samples)	> 1,000	> 1,000, 000	1,000 to 100,000	10-1,000	1-1,000

Table 2: *Main characteristics of printing processes*

The composition and rheological properties of printing inks are optimized for each process (table 3). Consequently, the printing deposits have different characteristics. The ink film thickness after drying is a crucial parameter in the printing electronics field, since it has a huge influence on specific properties such as conductivity.

Processes	Flexography	Gravure	Offset	Screen printing	Ink jet
Type of ink	Liquid	Liquid	Oil-based	Oil-based	Liquid
Ink vehicle	Solvents Water UV curable	Solvents Some with water	Oil based UV curable	Solvents	Solvents Water UV
Ink film thickness	6 to 8 µm	8 to 12 µm	1 to 2 µm	20 to 100 µm	1 to 2 µm
Ink viscosity (Pa.s)	0.01 to 0.1	0.01 to 0.05	5 to 50	0.1 to 10	About 10^{-2}
Limitations	Anilox clogging	Cells clogging	Oil-based Pasty ink	Limited particles size	Limited particles size

Table 3: *Characteristics of inks for conventional printing*

The electronics components have specific requirements in term of:

- deposition accuracy,
- amount of functional elements,
- and resolution (Blayo and Pineaux, 2005).

Two processes are remarkable:

- the screen printing for the high ink thickness it deposited,
- the ink jet for its high resolution.

Moreover, this process do not require printing form, hence it is easily handle and implemented by non-specialist in the printing field.

In addition of their remarkable ink film properties, ink jet and screen printing have some other technical advantages:

- they suit for small runs (table 3),
- their simple use allows their use by non-expert people,
- they print one sample at a time by only one printing group,
  - moreover, in order increase the amount of deposited ink, the ink transfer system mechanism can be repeated several times in order to superimpose layers of the same ink.

These two processes are adequate for research and development, or for small production.

Flexography and gravure processes have specific process parameters such as:

- their production cost. They require specific printing form,
- they are roll to roll techniques,
- they are dedicated to print thousands of samples each run (table 2),
  - the presses are composed of in-line printing groups. Consequently, each printing group deposes one ink layer. The superimposition of ink layers required the registering of the printing groups,
- they require expert handlers.

Hence, those processes are more relevant for large production and will be more and more studied as the development of printed electronics will grow.

Offset printing requires oil-based and pasty ink that are critical parameter for the formulation of functional inks.

Consequently, ink jet, screen printing and flexography were selected as potential relevant processes for manufacturing fuel cell components. They will be compared with spray and blade coating processes bellow by evaluating technical and economical characteristics of PEMFCs manufacturing.

3 PEMFC Manufacturing

In 1960 the first PEMFC was developed at General Electric by Thomas Grubb and Leonard Niedrach. They used sulfonated polystyrene electrolyte. Pratt & Whitney and General Electric were in charge of the power supplying of the NASA Gemini program, PEMFC were part of the Gemini V mission. The first improvements were made on the electrolyte with the incorporation of Teflon® between the catalyst layers and the electrolyte. The breakthrough was the innovation of the Nafion® polymer by Walther Grot working for DuPont de Nemour in the 1970s (Wang et al., 2011; Klein et al., 2005). The low operating temperature (80°C) and the possibility of quick start-up make the PEMFC a good candidate for transportation (Veziroglu and Macario, 2011) and portative applications. For all these reason, the PEMFC is focused in this article. The main drawbacks of this fuel cell technology are the catalyst, that is rare, noble and very expensive, the fuel cell intolerance to impure H_2 and its low operating temperature, that is an advantage for transportation and portative applications, is a drawback as well since it limits its efficiency by avoiding heat use.

3.1 PEMFC structure

A fuel cell power supply system is composed of a stack of individual Membrane Electrode Assembly (MEA) with a number function of the required power. Several MEAs are coupled in parallel separated by bipolar. The MEAs are multilayers composed by an electrolyte called a Proton Exchange Membrane (PEM), and by two electrodes that are made of a gas Diffusion Layer (GDL), closed to bipolar plate, and a Catalyst Layer (CL) (see figure 2).

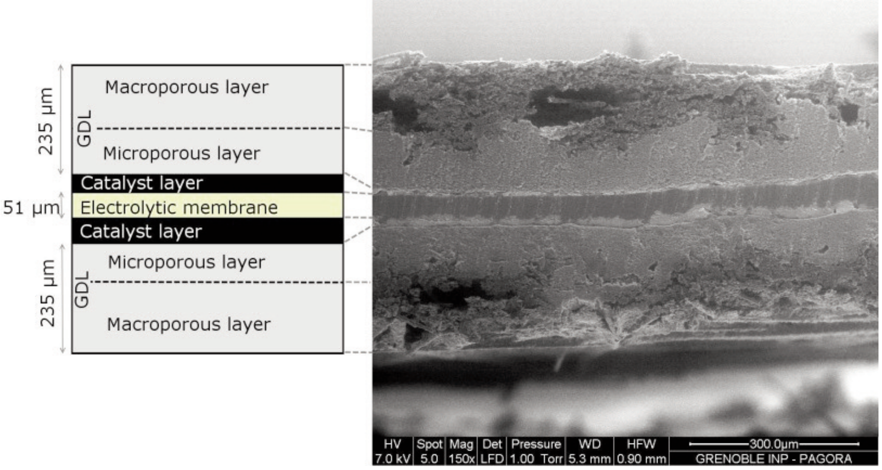


Figure 2: *Cross section of a Membrane Electrode Assembly: schematic representation (left) and its SEM observation (right) of a MEA composed of catalyst layers made by flexography (up CL) and blade coating (down CL)*

The **bipolar plates** provide

- an in-series electrical connection between the several cells,
- a physical separation between the cells, limiting the reactive gas mixing
- a structural support for the entire fuel cell
- a heat conduction from the active cells to a coolant
- a transport of gases toward the all surface of cell (Yua et al., 2011). Consequently, bipolar plate's material has to present several properties that have been measured by the U.S. DOE (Taherian, Golikand and Hadianfard, 2011).

Three main materials are suitable for bipolar plate manufacturing:

- graphite, although it has poor mechanical properties (Sharma et al., 2011; Yua et al., 2011),

- metals, even if it requires expensive surface treatment against corrosion (Dur, Cora and Koc, 2011),

- composites, but electrical conductivity problems may appear (Taherian, Golikand and Hadianfard, 2011; Wang et al., 2011).

Gas Diffusion layers (GDLs) are located at the interface between the bipolar plate and the Catalyst Layer (CL). Thus, this material insures the gas homogenisation from the bipolar plate channels to the catalyst layer, the water transport from the catalyst layer to the bipolar plates and the electrical conduction from the anodic catalyst layer to the bipolar plate and from the bipolar plate to the cathodic catalyst layer. It induces a specific

GDL structure and composition with in-thickness graded and interconnected properties such as porosity, permeability, transport, conductivity… (Cindrella et al., 2009) Consequently, the GDL is composed of a macroporous layer mainly made of carbon fiber cloth with polytetrafluoroethylen (PTFE or Teflon®), and a microporous layer of carbon nanoparticles in a Teflon® matrix.

In PEMFC, the electrolyte allows the transport of proton from the anode to the cathode, is it so called **proton exchange membrane**. It also avoids electron and reactants pathways from one side of the cell to the other. The Nafion® is composed of polyfluorosuflonic acid polymers (PFSA). It was the first material to be called ionomer. It is composed of a PTFE backone on which polyvynil alkyl ether pendant chains are grafted. The pendant chains are ended by sulfonated acid groups. The acid groups, that are highly hydrophilic, allows the protons (or the hydronium ions) to be attracted into the membrane core, and to be transported other in a water environment from one sulfonated group to another by the bending of one pendant chain toward another one (Jiao and Li, 2011).At the other side, the PTFE backbone has a highly hydrophobic character that is repelled by water. It leads to really particular structures and mechanisms occurring in the Nafion® depending on that water content. These phenomena's understanding is the core of numerous studies.

The electrochemical reactions at the anode *(2)* and the cathode *(3)* take place in the **catalyst layers**.

$$2H_2 \rightarrow 4H^+ + 4e^- \tag{2}$$

$$O_2 + 4H^+ + 4e^- \rightarrow 2H_2O \tag{3}$$

For both catalyst layers, the reactions require the presence in the same place of:

- the reactants (H_2 in anode, electron, protons and O_2 in cathode),
- a catalyst,
- an electron conductor,
- and a proton conductor.

Consequently, the catalyst layers are conceived for having good electron conductivity (with carbon powder), proton conductivity (with electrolyte) closed to catalysts such a system is called the triple point (Therdthianwong, Saenwiset and Therdthianwong, 2012). Moreover, the gas accessibility is managed with a specific structure that controls the water flow (Yu, Yuan and Sundén, 2011).

Finally, the fuel cell components that appear convenient to be manufactured by printing processes are:

- the microporous layers of the GDLs,
- and the catalyst layers.

As numerous issues are dealing with the catalyst layer, this element has been selected to validate the printing processes interest for manufacturing fuel cell components.

3.2 MEAs manufacturing

The MEAs manufacturing is the assembly of the five distinct layers and the bipolar plates that composed the cell. The catalyst layer can be produced by two techniques:

- by Catalyst Coated Membrane (CCM), where the catalyst layers are deposited onto the both sides of the membrane,
- by Catalyst Coated Backing (CCB), where a catalyst layer is transferred onto a GDL. This step is repeated twice to manufacture the two electrodes.

The deposition of the catalyst layers is made using inks or dispersion specifically formulated to incorporate the functional elements that are required for catalyst layers. The inks and dispersions are then transferred by the five processes previously mentioned:

- conventional processes for catalyst layer manufacturing,
- spray,
- and blade coating.
- printing processes selected in this article:
- ink jet,
- screen printing,
- and flexography.

Then, the three components are hot pressed at a pressure from 2 to 200 MPa and temperature from 120 to 195 °C during 50 to 300 s (Lin et al., 2009). These parameters are subjected to optimization (Therdthianwong, Manomayidthikarnb and Therdthianwong, 2007) in order to create intimate interfaces between the different layers by melting the ionomer of each layer that insures a continuous polymer matrix. Then, the fuel cell is built by stacking MEAs and bipolar plates.

3.2.1 Catalyst inks development

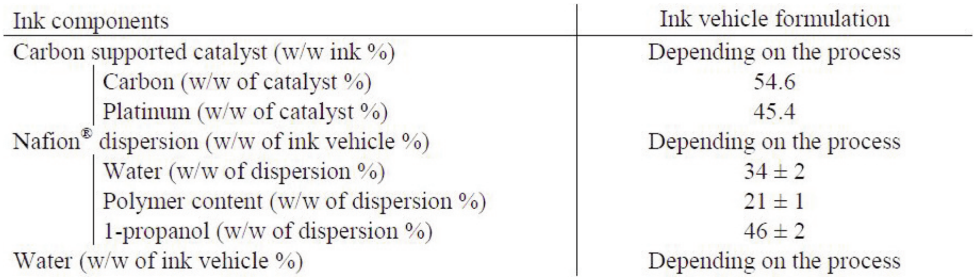
The formulation of inks for manufacturing catalyst layer requires taking into consideration:

- the substrate characteristics
- the process requirements
- and the final application: obtaining working catalyst layers with high performances and durability

The application requires avoiding the use of potential pollutants that could degrade the electrochemical characteristics of the catalyst layers. For this reason, the incorporation of additives is banished. The components that enter in the inks formulation are those that are required for achieving the electrochemical reactions, the water and the reactive gases transport into the cell:

- a catalyst, here platinum, where the electrochemical reactions take place
- an electron conductor. It is made of carbon nanoparticles that percolate to create a network. It conducts the electrons from their production sites (the catalysts of the anode part) towards the bipolar plate and from the bipolar plate toward their utilization sites (the catalysts of the cathode part).
- and a proton conductor, that is composed of Nafion® ionomer organized in a network that join up catalyst sites to the Nafion® membrane

The platinum is adsorbed onto the carbon nanoparticles, this material is called "carbon supported platinum" (Calvillo, 2011; Fraga, 2002). It insures the catalysis and the electron conduction. In conventional printing, an ink formulation can be adjusted by additives used in order to obtain the required rheological properties such as viscosity. In the case of printed electronics, and in catalyst layer manufacturing here, the functionalities are the most crucial ink properties and the additives use can be a problem. Water is a by-product of the reactions, thus it has been chosen as the ink vehicle. Therefore, the inks are made following the formulation given in table 4.

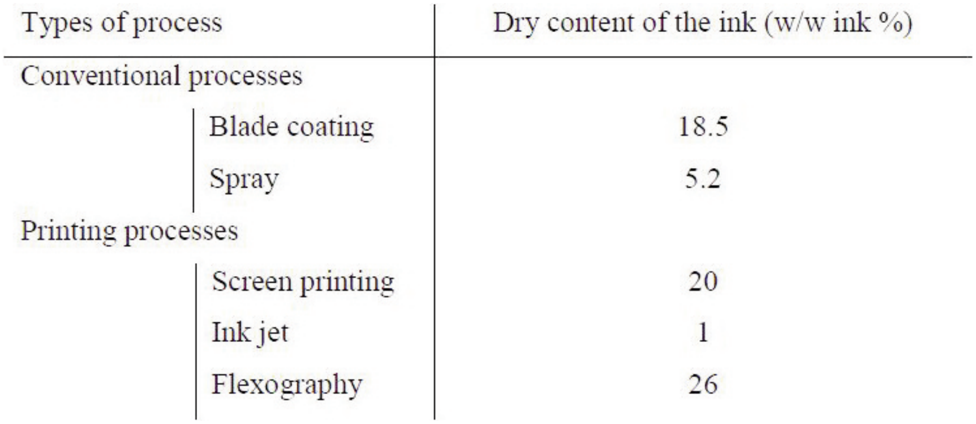


Ink components	Ink vehicle formulation
Carbon supported catalyst (w/w ink %)	Depending on the process
Carbon (w/w of catalyst %)	54.6
Platinum (w/w of catalyst %)	45.4
Nafion® dispersion (w/w of ink vehicle %)	Depending on the process
Water (w/w of dispersion %)	34 ± 2
Polymer content (w/w of dispersion %)	21 ± 1
1-propanol (w/w of dispersion %)	46 ± 2
Water (w/w of ink vehicle %)	Depending on the process

Table 4: *Ink formulation*

The process choice impacts rheological properties of the ink. The amount of functional particles in the ink is thus an important parameter. Moreover, the cost of these components can be significant. For these reasons, the ink is more conveniently described by its dry content. The dry content is adjusted to obtained sufficient ink processability as in table 5.

The dry content of the ink is composed of catalyst and Nafion® ionomers. The optimum ionomer content in the catalyst layer has already been focused in numerous works (Suzuki et al., 2011; Xie et al., 2010; Jeon, 2010; Kim et al., 2010; Ma and Solterbeck, 2009; Chaparro et al., 2009; Caillard et al., 2009). The ionomer content is given in weight by weight percentage (w/w %) as regards to the entire catalyst layer. In figure 3, this parameter is compared to the platinum loading of the catalyst layer. The platinum loading represents the weight by unit of surface. Traditionally, it is given in milligrams per square centimeter (mg cm-2). The anode and cathode platinum loadings are commonly equal to 0.2 and 0.4 mgPt cm-2 respectively.



Types of process		Dry content of the ink (w/w ink %)
Conventional processes		
	Blade coating	18.5
	Spray	5.2
Printing processes		
	Screen printing	20
	Ink jet	1
	Flexography	26

Table 5: *Dry content of the ink as regards to the process of deposition*

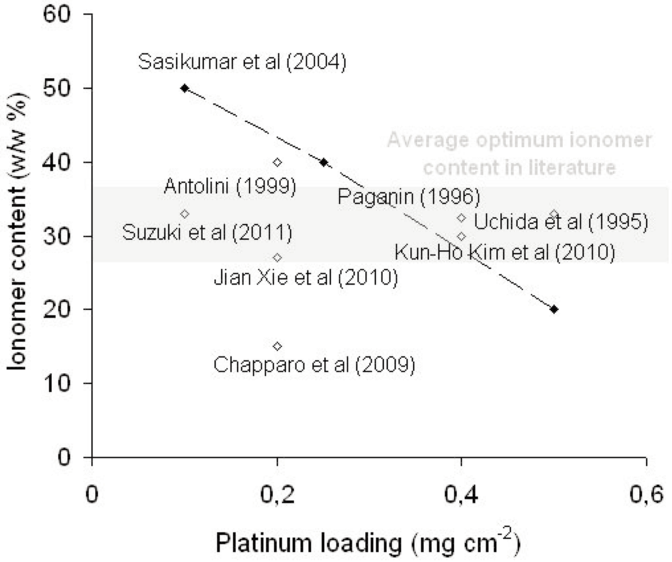


Figure 3: *Ionomer content as a function of the platinum loading of the catalyst layer*

The average ionomer content that is considered as a reference in the literature is around 30 w/w %. In figure 4, the ionomer content as a function of the Electrochemical Surface Area (ESA here in $m^2\ g^{-1}$) of platinum offers another way to choose the optimum ionomer content. The ESA indicates the surface of catalyst that is available to catalyze the electrochemical reactions in the catalyst layer. Once again, the best ESA values are obtained with an ionomer content around 30 w/w %.

Eventually, the formulation of the inks for each process can be calculated. However, even if the components have been chosen to limit the pollution risk, the use of water as the major ink solvent induces affinity problem. Hence, the catalyst layer can be made by CCB (by deposition on the GDL) or CCM (by deposition on the membrane) methods (see part 3.2). The two potential substrates are partly

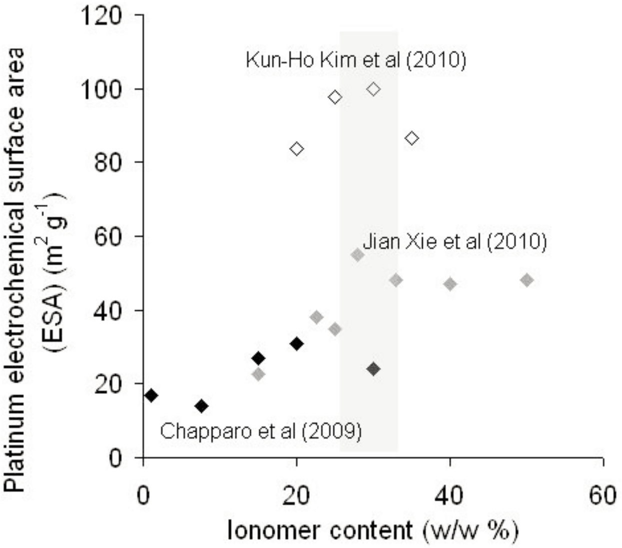


Figure 4: *Electrochemical Surface Area (ESA) of platinum as a function of the ionomer content in the catalyst layer*

composed of PTFE (see 3.1) that is a highly hydrophobic component. The affinity between the ink and the substrates has been quantified by apparent contact angle measures. A goniometer gives the measure of the initial contact angle of a 2 µ l fallen drop of probe solvents. In this study, only advancing contact angles were analyzed. The optical contact-measuring device (OCA 5) of (Dataphysics Instruments GmBH, Germany) provides a ± 0.2° reading accuracy. The used ink is formulated for flexography printing. As it has the highest ink dry content, it has the lowest amount of water into its formulation. Hence, its affinity is the best of the tested inks.

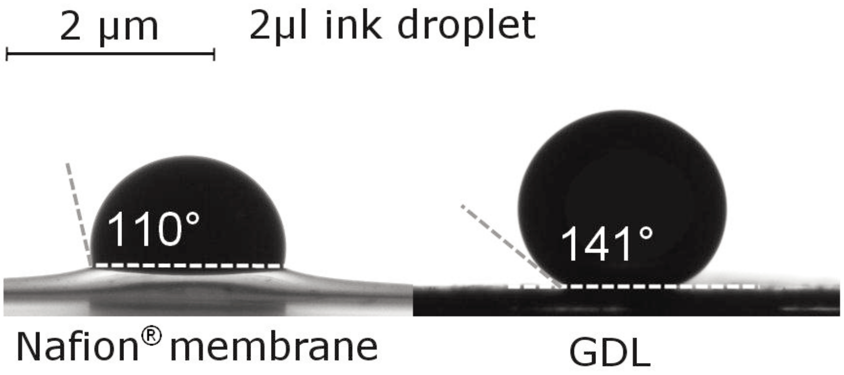


Figure 5: *Apparent contact angles of 2µ l ink drops deposited onto Nafion® and GDL*

As shown in figure 5, the apparent contact angle of the ink onto Nafion® and GDL are equal to 110° and 141°. They exceed the critical value of 90°, consequently, the affinity between the ink and the substrates is poor and can reduce the printability of catalyst layers.

3.2.2 Catalyst layers deposition protocol

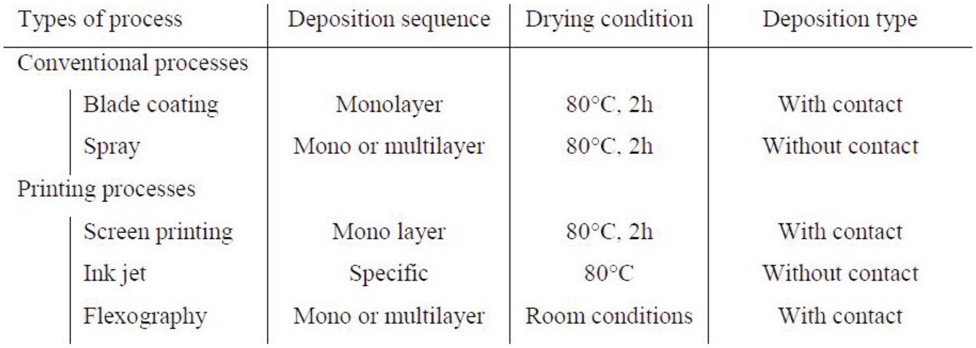
The protocol to manufacture catalyst layer depends on the process. Each process allows and requires different protocols that vary by their:

- Sequences of deposition. When catalyst layers are manufactured, the platinum loading is the targeted parameter, typically 0.2 and 0.4 mg_{Pt} cm^{-2}. The accurate platinum loading can be achieved either by the deposition of one layer (called monolayer in this study) or by superimposing several ink layer (multilayer).

- Drying conditions. The ink can be dried by temperature elevation that forced the vehicle evaporation or by can be placed in room conditions.

- Moreover, the process deposits the ink with or without contact between the ink and the substrate.

These parameters are detailed as a function of the process in the table 6.



Types of process	Deposition sequence	Drying condition	Deposition type
Conventional processes			
Blade coating	Monolayer	80°C, 2h	With contact
Spray	Mono or multilayer	80°C, 2h	Without contact
Printing processes			
Screen printing	Mono layer	80°C, 2h	With contact
Ink jet	Specific	80°C	Without contact
Flexography	Mono or multilayer	Room conditions	With contact

Table 6: *Characteristics of the manufacturing protocol of catalyst layers depending on the process used*

4 Characterization techniques

The characterization of the catalyst layer is performed by

- Scattering Electron Microscopy (SEM), for microstructure observations,

- and performance tests, for electrochemical characterizations.

4.1 SEM observations

Printing control protocol consists in SEM observation. Morphology of the catalyst layer deposited on GDL was characterized by optical and environmental scanning electron microscopy (ESEM) on a Quanta 200 FEI device (Everhart-Thornley

Detector). It is completed by a BackScattered Electrons detection (BSE). It consists of a high energy electron beam that reflects out of the sample detection volume. The peculiarity is that the heavy elements backscatter the incident electrons more strongly than the light elements. So, elements with a high atomic number (Z) appear brighter on the image. In this study, this technique allows a contrast of the platinum elements with an atomic number equal to 78 from the other elements existing in the catalyst and gas diffusion layers, namely: carbon (Z = 6), oxygen (Z = 8), fluorine (Z = 9) and sulphur (Z = 16).

4.2 Electrochemical performances of the catalyst layers

The tested catalyst layer is used as a cathode, the anode is a reference catalyst layer made by blade coating with a platinum loading equal to 0.2 mg_{Pt} cm^{-2}. A Nafion® NRE212 membrane is placed between anode and cathode as it is shown in figure 2. The MEA is placed between two gaskets and inserted between two bipolar plates. Humidified hydrogen and oxygen are fed into the cell at 100 RH%. The test is carried out at a cell temperature of 80 °C and at pressure of 1.5 Bar. A current density ramp is applied.

5 Comparison of the catalyst layers made by different deposition techniques

The comparisons of the catalyst layers made by the different deposition techniques are based on:

- Printing defects observation on the catalyst layer surfaces
- Electrochemical performances of MEAs composed by cathodes made by the depositions techniques
- Commercial expectations and issues

5.1 Printing defects observed on catalyst layers

Catalyst layers made by different deposition methods by CCB protocol are compared. For each process, samples with different platinum loading have been chosen in order to highlight the catalyst layers defects:

- deposition defects that are more visible on catalyst layer with a low platinum loading (from 0.02 to 0.2 mg_{Pt} cm^{-2}) and
- influence of the drying conditions on sample with higher platinum loading (from 0.2 to 0.5 mg_{Pt} cm^{-2}).

The samples are detailed in table 7 and the SEM observations of their surfaces are given from figure 6 to figure 15.

Types of process		Sample	Platinum loading ($mg_{Pt}\ cm^{-2}$)	Figure
Conventional processes				
	Blade coating	BC 1	0.22	Figure 6
		BC 2	0.46	Figure 7
	Spray	S 1	0.02	Figure 8
		S 2	0.20	Figure 9
Printing processes				
	Screen printing	SP 1	0.09	Figure 10
		SP 2	0.11	Figure 11
	Ink jet	IJ 1	0.10	Figure 12
		IJ 2	0.20	Figure 13
	Flexography	F 1	0.07	Figure 14
		F 2	0.18	Figure 15

Table 7: *Samples reference and characteristics*

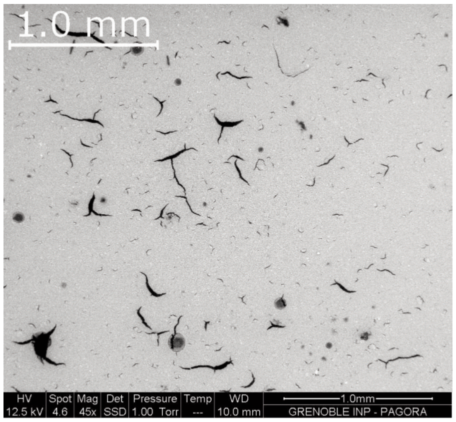


Figure 6: *Blade coated catalyst layer 0.22 mgPt cm*$^{-2}$ *(sample BC 1)*

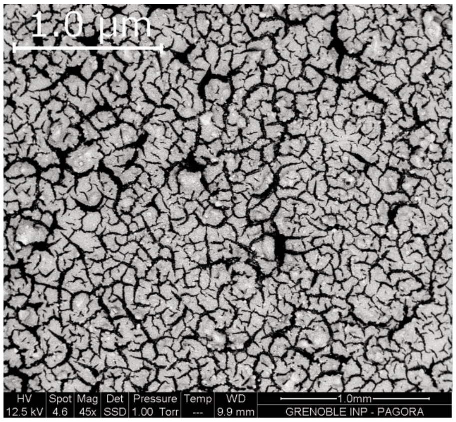


Figure 7: *Blade coated catalyst layer 0.46 mgPt cm*$^{-2}$ *(sample BC 2) (BSE)*

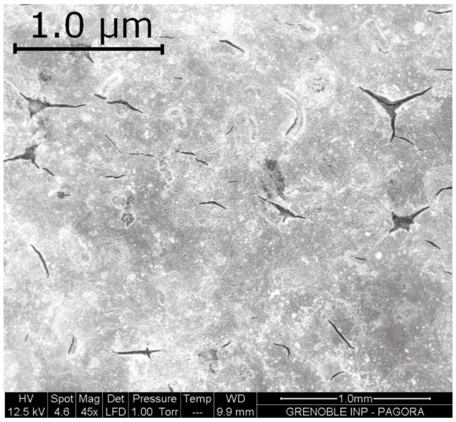


Figure 8: *Sprayed catalyst layer 0.020mgPt cm*$^{-2}$ *(sample S 1) BSE*

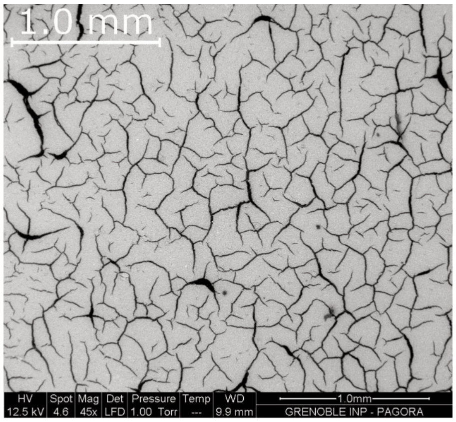


Figure 9: *Sprayed catalyst layer 0.20mgPt cm*$^{-2}$ *(sample S 2) BSE*

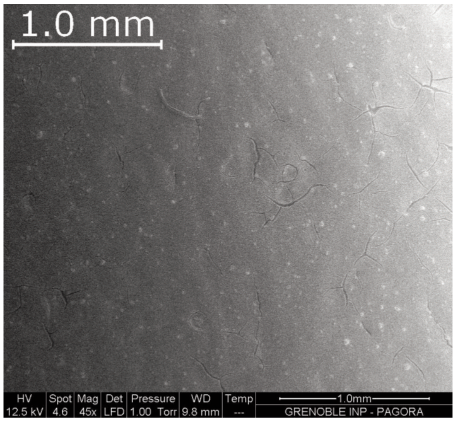


Figure 10: *Screen printed catalyst layer 0.09 mg_{Pt} cm^{-2} (sample SP1)*

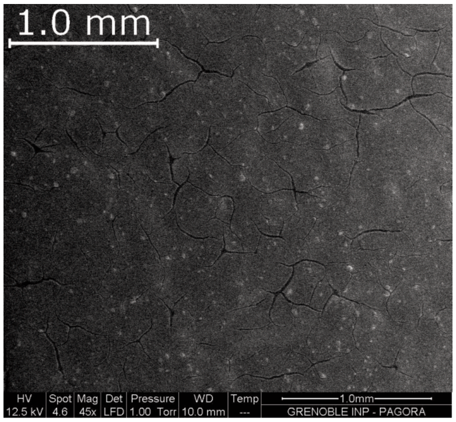


Figure 11: *Screen printed catalyst layer 0.11 mg_{Pt} cm^{-2} (sample SP 2) BSE*

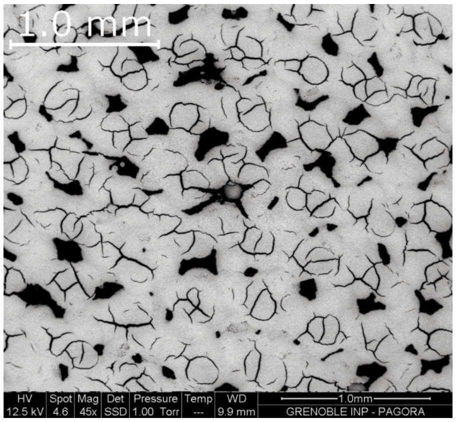


Figure 12: *Ink jetted catalyst layer 0.10 mg_{Pt} cm^{-2} (sample IJ 1)*

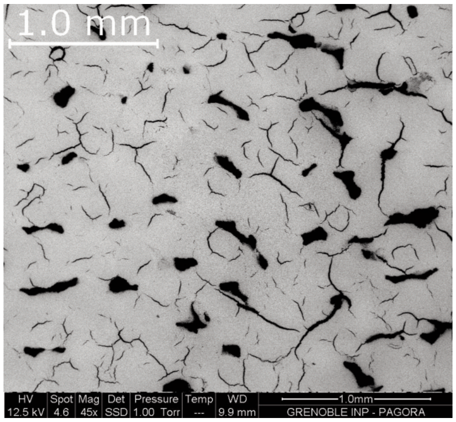


Figure 13: *Ink jetted catalyst layer 0.20 mg_{Pt} cm^{-2} (sample IJ 2)*

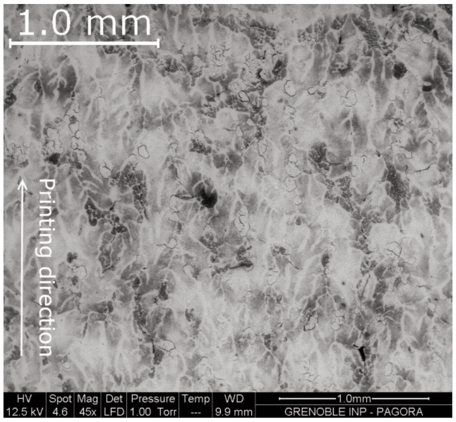


Figure 14: *Flexography made catalyst layer 0.07 mg_{Pt} cm^{-2} (sample F 1)*

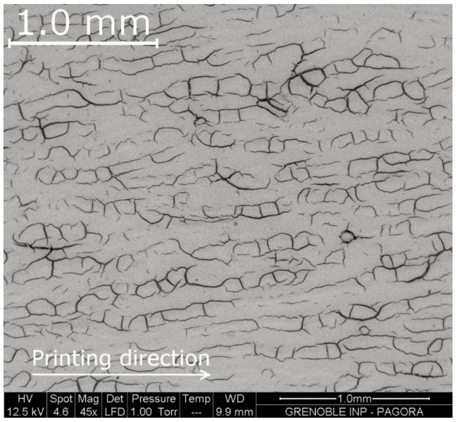


Figure 15: *Flexography made catalyst layer 0.18 mg_{Pt} cm^{-2} (sample F 2)*

The impacts of the deposition techniques on the catalyst layer surface (observed in the previous figures) will be compared as regards to the printability (5.1.1) and to the amount of ink that can be deposited (5.1.2).

5.1.1 Catalyst layer printability as regards to the deposition method

Blade coating, spray and screen printing

From figures 6 to 11, the catalyst layer made by blade coating, spray and screen printing show surfaces that are uniformly covered by the ink. Therefore, no printability problem can be deduced from these observations. In figures 10 and 11, no platinum heterogeneity is even shown by BSE technique on the screen printed catalyst layers. The catalyst layers made by such technique of deposition appear as having the better surface state.

On the contrary, the catalyst layers made by ink jet and flexography (figures 12 to 14) show specific printing defects that deal with printability issues.

Ink-jet

In figures 12 and 13, the surface of the catalyst layers manufactured by ink jet process has some lack of ink. Moreover, excess of ink seems to be frequently localized where the ink drops were ejected onto the GDL. The drops had not a sufficient affinity with the substrate to spread and then to form a continuous ink film.

Flexography

Figure 14, the surface of the catalyst layer made by flexography show a printing defect called marbling. This defect typically occurs when the affinity between the ink and the substrate is poor as confirmed by the contact angle measurements (see 3.2.1). The scission of the ink film in the nip zone is not favorable to deposit the ink onto the substrate, and consequently, the ink is not uniformly transferred. Lines with higher amount of ink appear parallel to the printing direction.

5.1.2 Influence of the amount of ink

A comparison of the minimum and maximum platinum loadings of these samples shows that:

- the blade coating can achieve catalyst layers with low platinum content (< 0.2 mg_{Pt} cm^{-2}),
- the spray, ink jet and flexography are not suitable to deposit a high amount of platinum (> 0.2 mg_{Pt} cm^{-2}).

Moreover, figure 12 highlights the surface of a catalyst layer made by the deposition of a really low amount of ink (0.02 mg_{Pt} cm^{-2}) onto a GDL by the spray method. At such low loading, the platinum is not uniformly deposited onto the surface.

Consequently, the minimum platinum loading is limited by (i) the deposition process but also by (ii) a minimum ink quantity that is sufficient to deposit ink on the all catalyst layer surface.

Influence of the multilayer protocol in flexography

The influence of the amount of ink on the catalyst layer surface is also observable on the samples made by flexography. The samples of figures 14 and 15 are made by the superimposition of ink layers. Figure 14 is the surface of catalyst layer made by the deposition of one ink layer and figure 15 by the superimposition of five ink layer. In order to highlight the influence of the number of ink layers that was superimposed to manufacture these catalyst layers, figure 16 shows the BSE pictures of the surface of catalyst layers. They are made by flexography by the superimposition of 1, 2, 3 and 5 ink layers.

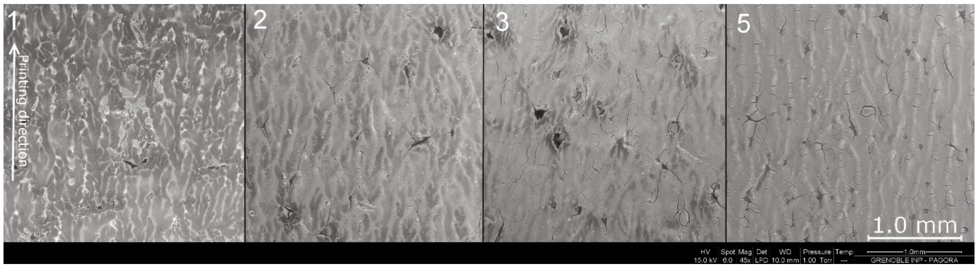


Figure 16: *Catalyst layer made by flexography by the superimposition of 1, 2, 3 and 5 ink layers (BSE)*

The platinum appears brighter in the picture than the other catalyst layer components. The marbling defect previously observed is also visible. The less amount of ink, the more the marbling is visible. The platinum is non-uniformly deposited due to the marbling defect. Then, the more ink layers are superimposed, the less platinum non uniformities are observable. It means that the BSE detector find enough platinum on the all surface. However, it does not indicate a uniform deposition of ink on the GDL.

Cracks formation on the catalyst layer

In figure 15, a second major defect is observable: the layer cracks. Crack structure and modeling is the topic of numerous studies since material desiccation is a common issue (Cohen, Mathiesen, and Procaccia1, 2009). Mud cracks (Gaul, Weber and Rethmeier, 2011), polymer (Weh, and Venthur, 2004), and calcium carbonate paste (Kitsunezaki, 2009) drying has been investigated. The layer thickness is a major parameter in cracks formation. It is visible when comparing figures 6 and 7, figures 8 and 9, figures 10 and 11 and figures 14 and 15: for each process, an increase of the amount of ink, leads to thicken the catalyst layer and then to increase the cracks formation. Due to gradients of solvent evaporation or temperature, the layer structure is submitted to tensile stresses. The energy is released by structure brakes. Heterogeneities are described as brake precursors in the case of shrinkage-cracks. Indeed, a strong heterogeneity does exist: the marbling patterning. In figure 15, the peak to peak distance between two inked lines is measured on pictures of one layer of ink. It is equal to 76 ± 13μ m, while the crack width, measured on figure 14, is equal to 83 ± 10μ m. The similarity between the marbling and crack geometries tends to confirm that the shrinkage-cracks are mainly formed following the marbling inhomogeneity.

If all the samples are covered by numerous cracks, although the screen printed samples (figures 10 and 11) are rarer.

5.2 Electrochemical performances

The performances of cathodes made by the different deposition techniques, blade coating, spray, ink jet, screen printing and flexography techniques, are reported in figure 17.

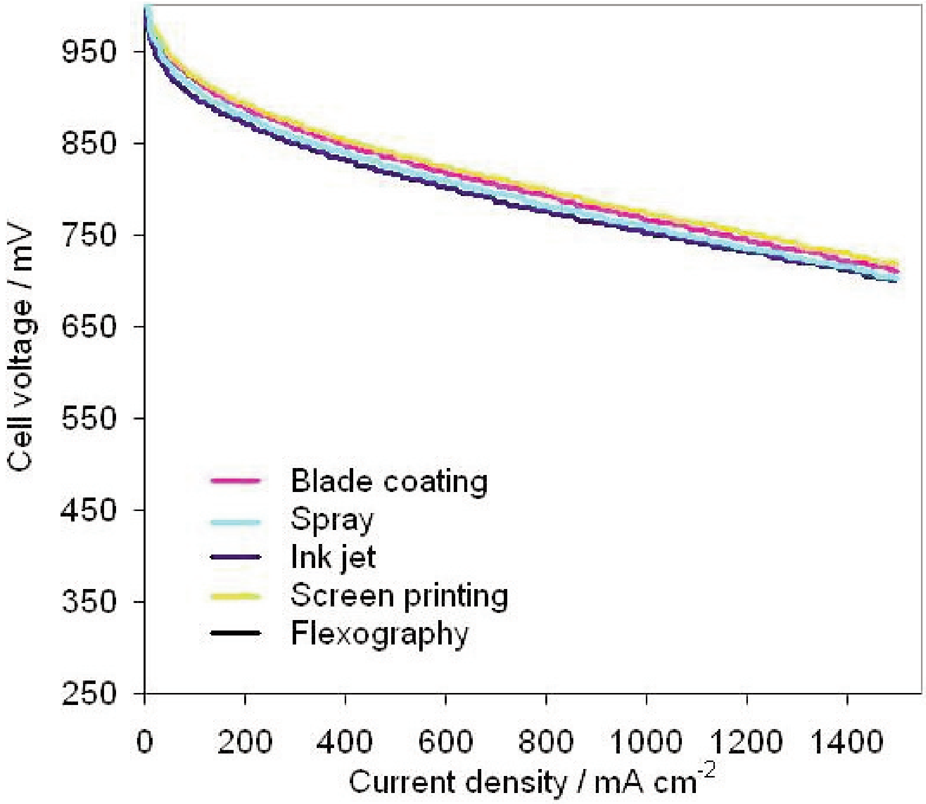


Figure 17: *Performances of catalyst layers made by blade coating, spray, ink jet, screen printing and flexography techniques*

This figure highlights the behavior of cells composed of cathodes that were made by the five processes. Their performances are similar. Consequently, the deposition techniques and the protocol of deposition are not the primary parameters that influence the catalyst layer performances. For the following parts of this article, the catalyst layers will be considered as having close performances as regards to their manufacturing techniques.5.3 Commercial issues

5.3.1 Industrial and market expectations

In a context of fossil fuel shortage and in pollutant reduction, such as the Kyoto protocol that regulates the green house reduction, technologies that combine new energy sources and sustainable behavior have an increasing demand. Consequently, solar and fuel cells are targeted technologies (Sopian and Wan Daud, 2006).

Fuel cell market grew from $ 353 million in 2005 to $ 498 million in 2009. The future trend is estimated to reach 1.2 billion by 2014. For example, the U.S. DOE described in the 2010 FUEL CELL TECHNOLOGIES MARKET REPORT a Japanese target of a production of 2 million of fuel cell equipped vehicles for 2025.

5.3.2 Production of catalyst layers made by printing processes

Manufacturing catalyst layers can be achieved by different types of process. It has been demonstrated before, that the catalyst layer show different structure, but similar performances as regards to their manufacturing process.

In conventional printing, for example, each process is dedicated to specific kind of production. Therefore, to choice of the optimum process for catalyst layer production depends on the production type.

The fuel cell market should be multiplied by ten from 2005 to 2014 (see part 5.3.1). Consequently, the total demand on surface area of catalyst layer follows this trend.

Moreover, the targeted applications cover portative, transport and power supply. The required geometry of catalyst layers is then different by applications and by company.

In fuel cell field, one of the major concerns is the raw material cost since it varies from 70 to 90 % of the catalyst layer cost. The two components that have the higher cost are:

- The platinum. The increase in platinum demand should thus increase its rate in the market. Moreover, the decrease in platinum use in the catalyst layer is an interesting solution. However, it is risky and may diminish the performance and durability characteristics of the cell.

- And the Nafion® membrane. The Nafion® membrane (made of polyfluorosuflonic acid polymer PFSA) as the contrary to the platinum, an increasing demand in Nafion® may leads to increase the number of PFSA membrane manufacturers. Nowadays, the undisputed leader in PFSA manufacturing is Dupond™.

In figure 18, the manufacturing cost per unit of surface (\$ m^{-2}) of catalyst layer is estimated. It has been compared as regards to the deposition system chosen for a production that varies from 1,000 to 100,000 m^2 per year. It incorporates, among other parameters, the raw material cost (supposed constant), production cost, and the process specifications.

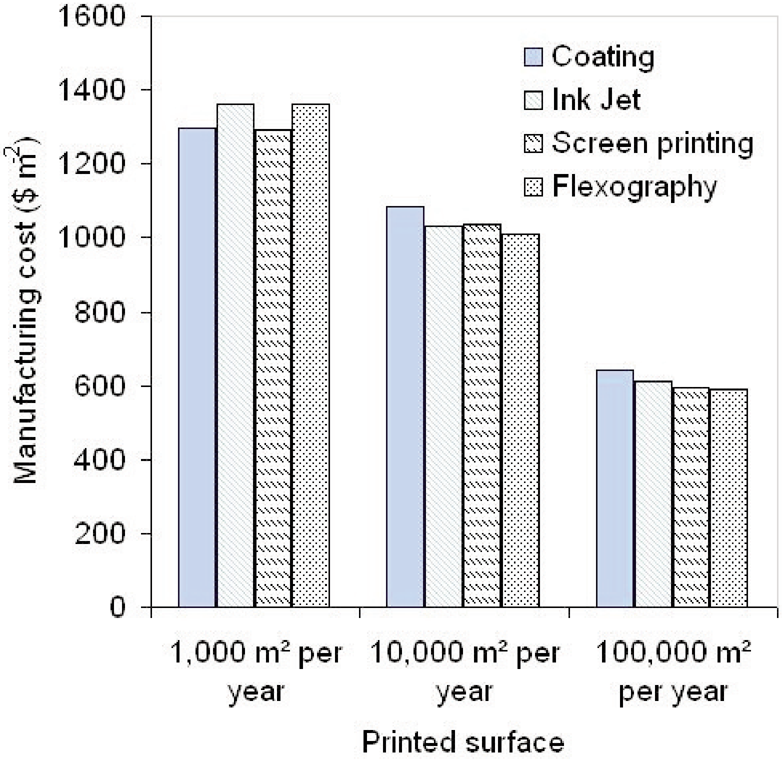


Figure 18: *Manufacturing cost of catalyst layer by different processes as a function of the surface area produced*

In figure 18, the global trend of manufacturing cost decreases with the increase of the production of catalyst layers (by surface area). This mainly indicates raw material cost diminishing. At 1,000 m^2 per year of catalyst layer, coating and screen printing appears as the most interesting technology of production. At 100,000, flexography and screen printing seem to be more financially relevant, even if the screen printing is not conventionally dedicated to big production.

This graph follows the trend of the deposition processes development: for the moment, blade coating is preferentially used, and the development of new technology focuses on more continuous process such as the flexography.

Conclusion

This article focuses on the technical and commercial issues that drive the catalyst layer manufacturing for PEM fuel cell.

The deposition techniques have an important influence on the catalyst layer surface structure. However, no crucial differences have been found considering the performance values of the tested catalyst layers. The main distinctions deal with:

- Technical issues:
- the minimum and maximum amount of ink that can be deposited (calculated in platinum loading mg_{Pt} cm^{-2}),
- the possibility to structure the catalyst layer using multilayer protocol and pattern,
- Commercial issues:
- the possibility to developed catalyst layers technology, by rapidly modifying the deposition protocol,
- the optimum surface area of production for limiting the production cost per year,
- and finally, the technical qualification requires to use the process.

The commercial and technical issues are crossed in table 8 where processes that fulfilled the parameters listed below are then given.

In this table, the printing processes are well placed. They allow manufacturing all kind of catalyst layers at different level of production. The ink jet appears as adequate for catalyst layer development. The screen printing allows the production of little to large surface area of catalyst layers (from some samples to some 100,000s). Finally the flexography seems to be dedicated to large production of special catalyst layer that require structuration.

This work should be enhanced by studying the influence of the drying conditions of each kind of deposition technique. Moreover, the drying has a strong influence on cracks formation. Moreover, the durability of the cells have to be tested to obtain a complete active layer characterization and then to validate a deposition process.

		Allows rapid development (no printing plate)	Optimum surface area (m^2 per year)			Manipulator expertise	
			1,000 and less	around 10,000	100,000 and more	Low	Expert
Platinum loading ($mg_{Pt}\ cm^{-2}$)	< 0.2	Ink jet	Screen printing	Flexography Screen printing Ink jet	Flexography Screen printing	Ink jet Screen printing	Flexography
	> 0.2	Coating	Coating Screen printing	Screen printing	Screen printing	Coating Screen printing	
Catalyst layer structuration		Ink jet		Ink jet Flexography	Flexography	Ink jet	Flexography

Table 8: *Best deposition techniques as regards to the commercial and technical issues*

The improvements in fuel cells that were developed after 1970 targeted:

- the suppression of diffusion limitation in the electrodes,
- the decrease the catalyst cost,
- and the increasing the performances and durability.

The contribution of the printing processes on the fuel cell development should be more and more noticeable in a near future.

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